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## Citation

Kim, Hoon, Harish B. Bhandari, Sheng Xu, Roy G. Gordon. 2008. Ultrathin CVD Cu seed layer formation using copper oxynitride deposition and room temperature remote hydrogen plasma reduction. *Journal of The Electrochemical Society* 155, no. 7: H496-H503.

## Published Version

<http://dx.doi.org/10.1149/1.2912326>

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## Ultrathin CVD Cu Seed Layer Formation Using Copper Oxynitride Deposition and Room Temperature Remote Hydrogen Plasma Reduction

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Cu seed layers for future interconnects must have conformal step coverage, smooth surface morphology, and strong adhesion. Conformal deposition had been achieved by chemical vapor deposition (CVD), but CVD Cu films have rough surfaces and poor adhesion. In this paper, conformal, smooth, adherent, continuous, and thin (<9 nm) Cu films were made by CVD. CuON was deposited from a Cu-amidinate precursor, H<sub>2</sub>O, and NH<sub>3</sub> at 140–180°C on Ru. Crystallites in the deposited film have either a Cu<sub>2</sub>O or Cu<sub>3</sub>N structure depending on the ratio of H<sub>2</sub>O to NH<sub>3</sub>. As-deposited CuON films have a smooth surface morphology [ $\sim 0.5$  nm root-mean-square (rms) roughness] and are highly conformal (>95% step coverage in 40:1 aspect ratio holes). The CuON films were then reduced with remote hydrogen plasma near room temperature to minimize agglomeration of the thin Cu films during reduction. After reduction, CuON films having a Cu<sub>2</sub>O crystal structure showed a higher density Cu film (95%) than those having a Cu<sub>3</sub>N crystal structure (84%). Both reduced Cu films had a smooth morphology ( $\sim 1$  nm rms roughness). Thus, deposition of a CuON film having a Cu<sub>2</sub>O crystal structure and then reduction with remote hydrogen plasma can make Cu layers that can serve as seed layers of future Cu interconnects.

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Manuscript submitted January 18, 2008; revised manuscript received February 15, 2008. Available electronically May 5, 2008.

Cu is used as the interconnect material for ultralarge-scale integrated circuits due to its low resistivity and excellent stability against stress migration and electromigration. Cu is filled by electrochemical deposition (ECD), which has the merits of a low process temperature, a high deposition rate, a cost effective process, and a complete via filling capability. This ECD method requires a thin Cu seed layer as an electrode. In current technology, the Cu seed layer is deposited by sputtering on Ta over a TaN diffusion barrier. However, beyond the 45 nm generation, sputtering cannot cover the sidewalls of vias and trenches uniformly due to its poor step coverage, which results in void formation during ECD and a reduced durability of interconnects.<sup>1</sup> Thus, a conformal deposition method for Cu seed layer deposition is required.<sup>2</sup> Chemical vapor deposition (CVD) and atomic layer deposition (ALD) are well-known methods of conformal Cu seed layer deposition.<sup>3–9</sup> From the viewpoint of productivity, CVD is the most promising candidate for Cu seed layer deposition. For the 32 nm generation, considering the metal linewidth ( $\sim 32$  nm) and the thickness of the barrier/cladding (2.4 nm), a conformal, smooth, adherent, and continuous CVD Cu seed layer less than 10 nm thick is required.<sup>10</sup>

To deposit 10 nm of continuous CVD Cu, new underlayers should be considered because Ta/TaN underlayers cause a rough morphology and poor adhesion.<sup>4,5</sup> Ru is an air-stable metal with a low resistivity and no solubility in Cu, and it does not form any intermetallic compounds with Cu.<sup>11</sup> More importantly, Ru has a strong adhesion to CVD Cu compared with Ta or TaN.<sup>6,7,12,13</sup> Although Cu has a fairly high wettability on Ru, 10 nm of continuous CVD Cu seed layer cannot be deposited on Ru, because metallic Cu made by CVD has typical three-dimensional (3D) island growth and requires a thickness of at least 20 nm to form a continuous layer.<sup>5</sup>

To deposit a thin (<10 nm), smooth, and continuous CVD seed layer, a different approach is required. Cu compounds, such as Cu oxide or nitride, have a better wettability than metallic Cu, which results in a higher nucleation density, and continuous thin layers with a smoother and more continuous morphology than metallic Cu. There is a report of CVD Cu<sub>2</sub>O deposition for seed layer application.<sup>14</sup> However, the reduction process temperature is 275°C, which is too high to form a thin, continuous, and smooth seed layer for future Cu interconnect processing. The Ta underlayer used for that experiment is oxidized during oxide deposition, which de-

creases the adhesion strength of Cu to Ta and increases the contact resistance. Thus, there is need for a new precursor having a low deposition temperature and a new underlayer that can be easily reduced. Deposition of Cu<sub>3</sub>N can also be a good candidate. ALD Cu<sub>3</sub>N deposition and reduction shows the possibility of thin seed layer fabrication,<sup>15,16</sup> but ALD is too slow for large-scale production. The reported CVD process for Cu<sub>3</sub>N required a high deposition temperature (400°C) and it did not mention the morphology, which is most important in this application.<sup>17</sup>

Reduction of a deposited Cu<sub>2</sub>O or Cu<sub>3</sub>N film to copper metal must be done at a low enough temperature to avoid agglomeration of the Cu. The reduction of a Cu oxide or nitride at too high a temperature produces rough and discontinuous Cu films.<sup>14,15,18,19</sup> Thus, the reduction of Cu compounds should be conducted at as low a temperature as possible to maintain the smooth and continuous morphology of as-deposited Cu compound films.

In this study, we deposited Cu oxide, nitride, and oxynitride (CuON) using CVD, and then these compounds were compared from the viewpoint of morphology and film density before and after reduction to copper metal. A Cu amidinate, (*N,N'*-di-*sec*-butylacetamidinato)copper(I) dimer (abbreviated [Cu(<sup>t</sup>Bu-Me-amd)]<sub>2</sub>), was used to decrease the deposition temperature. This precursor's reactivity at a low substrate temperature has been reported under ALD conditions.<sup>9,15</sup> Cu oxide, Cu nitride, and CuON are formed by using Cu amidinate with H<sub>2</sub>O and NH<sub>3</sub> as reactant gases.

The Cu compound films were then reduced by H<sub>2</sub> remote-plasma treatment because atomic hydrogen is one of the strongest reducing agents, which can enable room temperature reduction and minimize agglomeration of the copper.<sup>19,20</sup> Cu<sub>2</sub>O reacts with atomic hydrogen to form pure Cu and water by the following reaction



Provided that no kinetic limitations exist, this reaction will occur because the Gibbs energy change of this reaction is  $-118.3$  kcal/mol at 25°C.<sup>21</sup> Thus, Cu<sub>2</sub>O might be reduced with atomic hydrogen even at room temperature.

In this work, we found that the crystal structure of as-deposited CuON films differed depending upon the ratios of H<sub>2</sub>O to NH<sub>3</sub> during depositions. A high H<sub>2</sub>O ratio makes films with a Cu<sub>2</sub>O crystal structure, while a high NH<sub>3</sub> ratio makes a Cu<sub>3</sub>N crystal structure. Even though a film has a Cu<sub>2</sub>O or Cu<sub>3</sub>N crystal structure, both oxygen and nitrogen are incorporated in the film when a mixture of H<sub>2</sub>O and NH<sub>3</sub> is used as a reactant gas during deposition. However,

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the overall deposition rate of the film is mainly determined by the  $\text{H}_2\text{O}$  flow rate. CuON film shows a smooth surface morphology [root-mean-square (rms) roughness  $< 1$  nm]. CuON films having  $\text{Cu}_2\text{O}$  structure have higher density than films having  $\text{Cu}_3\text{N}$  structure. After 1 min reduction with  $\text{H}_2$  remote plasma at room temperature, both films are fully reduced to Cu metal that has smooth morphology (rms roughness  $\sim 1$  nm) and low resistivity ( $12 \mu\Omega \text{ cm}$  at 9 nm thickness). CVD CuON films having  $\text{Cu}_2\text{O}$  structure form Cu with higher density after reduction than CuON films having  $\text{Cu}_3\text{N}$  structure do. Room temperature remote hydrogen plasma reduction is the best method to maintain smooth surface morphology. Thus, this process can be a promising candidate of thin CVD Cu seed layer deposition for future Cu interconnects.

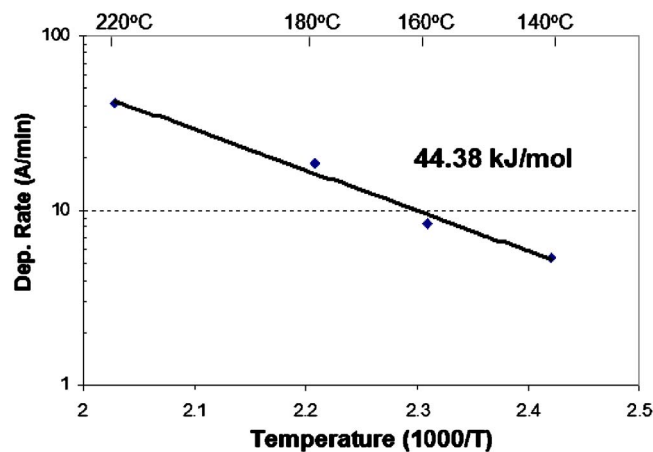
### Experimental

The deposition of CuON was done in a tube-furnace type reactor which has 36 mm inner diameter (i.d.). Copper (I)  $N,N'$ -di-*sec*-butylacetamidinate ( $[\text{Cu}(\text{Bu-Me-amd})]_2$ ) was used as a Cu precursor, which was delivered by bubbling with 40 sccm of  $\text{N}_2$  carrier gas. The bubbler temperature was  $130^\circ\text{C}$ , which maintained the Cu precursor as a liquid phase because its melting point is  $77^\circ\text{C}$ . All the gas lines, bubbler, and valves were located in an oven which maintained a good temperature uniformity.  $\text{H}_2\text{O}$  was used as an oxygen source, which was evaporated from a reservoir at room temperature without any carrier gas. The flow rate of water vapor was controlled by a needle valve that was calibrated by comparing with the pressure increase of the chamber by a measured  $\text{N}_2$  flow rate.  $\text{NH}_3$  was supplied as a nitrogen source whose flow rate was controlled by a mass flow controller. The total flow rate of reactant gases ( $\text{H}_2\text{O}$  and  $\text{NH}_3$ ) was maintained at 40 sccm, and the ratio of  $\text{H}_2\text{O}$  to  $\text{NH}_3$  was set to the values 40:0, 30:10, 20:20, 10:30, or 0:40. The reaction gases were mixed with Cu precursor vapor in a small (5 mm i.d.) tube just prior to entering the reactor tube (36 mm i.d.) to ensure thorough mixing. The films were deposited at substrate temperatures from 140 to  $220^\circ\text{C}$  under a total chamber pressure of 8 Torr. The films were reduced with  $\text{H}_2$  remote plasma, which heated the substrates from room temperature to temperatures as high as  $50^\circ\text{C}$ . A toroidal plasma generator (ASTRON I type AX7670, MKS) was supplied with 180 sccm of Ar for plasma ignition and 200 sccm of  $\text{H}_2$ , which upon dissociative excitation acted as a reducing agent. The reduction time was varied from 30 to 180 s. A Si wafer with a 100 nm thermal oxide was used as the substrate. Ru was deposited by sputtering to a 20 nm thickness and exposed to the atmosphere prior to CVD.

The surface morphologies of the as-deposited CuON and reduced films were evaluated by an atomic force microscope (AFM, Asylum MFP-3D AFM). The thickness and composition of the deposited films were measured using 2 MeV  $\text{He}^+$  Rutherford backscattering spectroscopy (RBS). The physical thicknesses of CuON and reduced Cu films were measured by AFM after making stripe patterns by photolithography and etching in dilute nitric acid. CuON and Cu films were etched with nitric acid diluted by deionized water in a volume ratio 1(acid):40(water) or 1:10, respectively. The resistivities of reduced Cu films were evaluated by a four-point probe (Miller Design & Equipment FPP-5000). The phases of as-deposited Cu oxynitride and reduced films were evaluated by transmission electron microscopy (TEM) diffraction (JEOL JEL2010 TEM) using as a substrate a 50 nm thick  $\text{Si}_3\text{N}_4$  membrane TEM grid (Ted Pella, Inc., prod. no. 21500-10).

### Results and Discussion

*Cu oxynitride deposition with  $[\text{Cu}(\text{Bu-Me-amd})]_2$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$ .*— *Temperature effect on CuON film deposition.*— CuON was deposited from  $[\text{Cu}(\text{Bu-Me-amd})]_2$  vapor and a mixture of  $\text{H}_2\text{O}$  vapor and  $\text{NH}_3$  gas. Figure 1 shows the deposition rate of Cu oxynitride at different deposition temperatures. The ratio of  $\text{H}_2\text{O}$  flow to  $\text{NH}_3$  flow was 30:10 in these depositions. The deposition rate increased with increasing deposition temperature, up to a value over



**Figure 1.** (Color online) Arrhenius plot of CuON deposition rate from  $[\text{Cu}(\text{Bu-Me-amd})]_2$  vapor and a mixture of 30 sccm of  $\text{H}_2\text{O}$  and 10 sccm of  $\text{NH}_3$ .

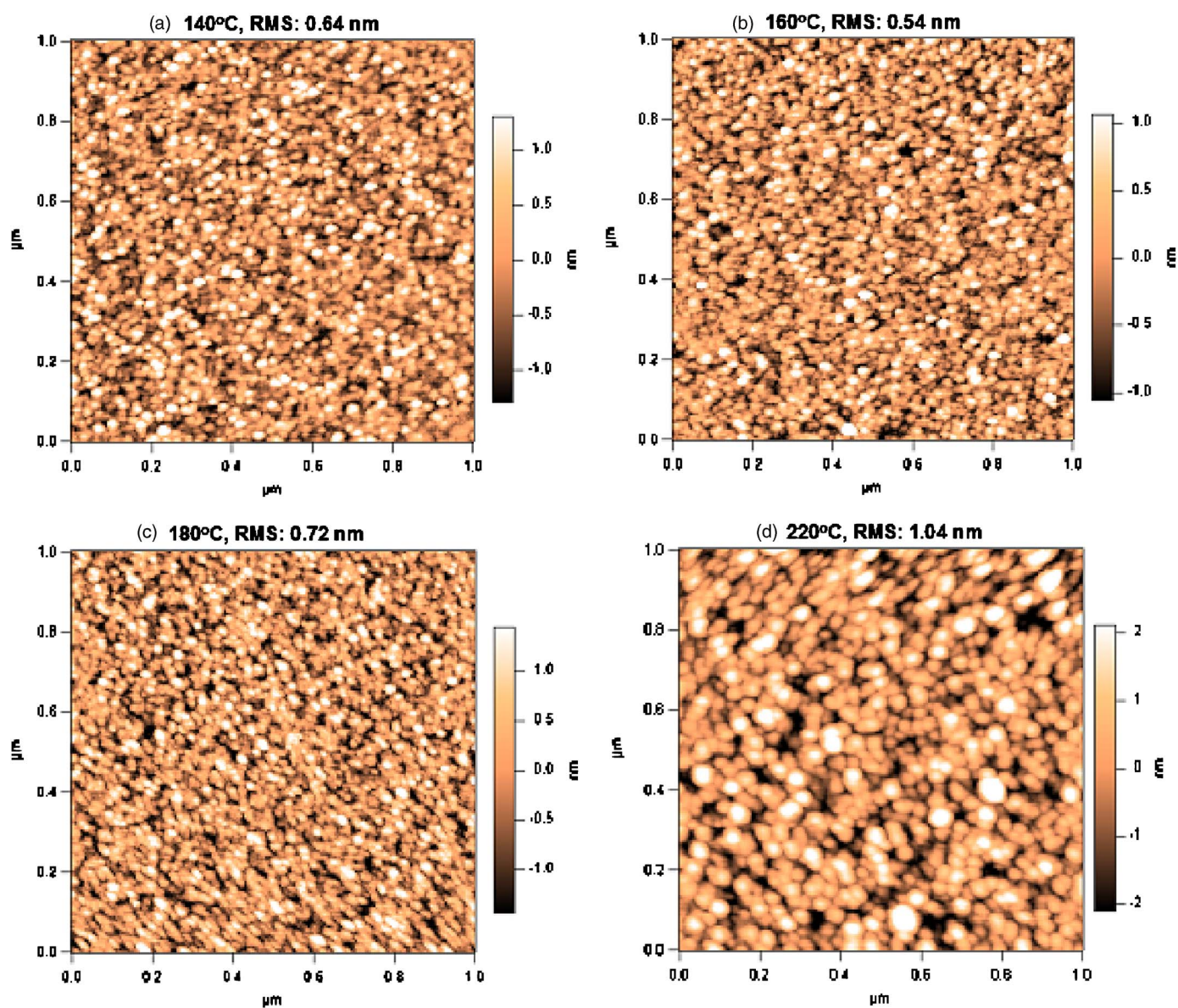
4 nm  $\text{min}^{-1}$ . Over the range of temperature studied ( $140$ – $220^\circ\text{C}$ ), the deposition rate has an Arrhenius form, which means that the CVD reaction is kinetically controlled in that temperature range. The activation energy of this reaction was found to be 44 kJ/mol.

The morphology of CuON depends on the deposition temperature, as shown in Fig. 2 for films with thicknesses about 20 nm. These films are all smooth, with a rms roughness  $< 1$  nm. The smoothest film was deposited at  $160^\circ\text{C}$ , with a roughness of only 0.5 nm, which is just slightly larger than the roughness of the Si substrate. The surface grain size of CuON is constant at about 20 nm up to a deposition temperature of  $180^\circ\text{C}$ . At  $220^\circ\text{C}$ , some large particles 400–600 nm in diameter were observed on the film surface, although the film still had a smooth surface morphology (rms roughness 1.04 nm) and a fairly small grain size ( $\sim 40$  nm). These particles seemed to be formed by gas-phase reaction at the highest temperature. Thus, CuON for a seed layer can be deposited over the temperature range from about  $140$ – $180^\circ\text{C}$  from the viewpoint of surface morphology. This result is different from the temperature effect on morphology of  $\text{Cu}_2\text{O}$  and  $\text{Cu}_3\text{N}$ . The morphology of pure Cu compounds such as  $\text{Cu}_2\text{O}$  and  $\text{Cu}_3\text{N}$  was very sensitive to deposition temperature.<sup>15,19</sup> A deposition temperature only 30 or  $40^\circ\text{C}$  higher than the optimized condition always made films with a rough morphology in the deposition of pure Cu compounds. However, CuON is less affected by deposition temperature, so smooth CuON films are obtained over a wider process window than for  $\text{Cu}_2\text{O}$  or  $\text{Cu}_3\text{N}$  films.

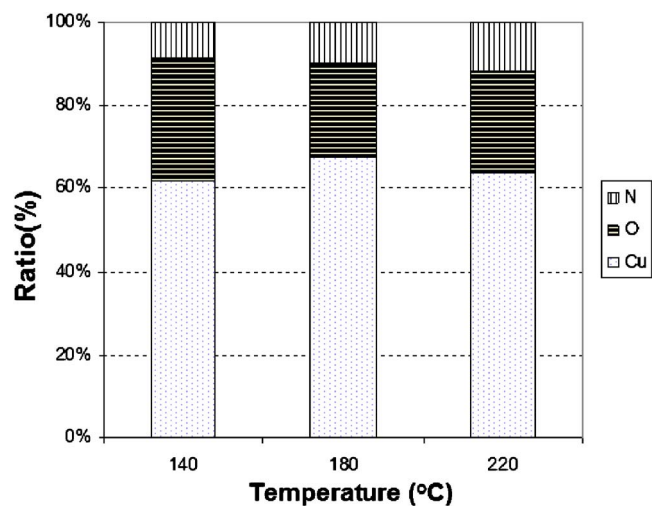
The composition of CuON deposited at different temperatures is shown in Fig. 3. The atomic percentages of Cu, O, and N are compared at 140, 180, and  $220^\circ\text{C}$  as measured by RBS for films deposited on amorphous carbon substrates. The composition does not change much over that temperature range, which means that CuON is a stable phase under these deposition conditions. Thus, CuON has a relatively wide process window in which to get a uniform composition and morphology because it is less sensitive to the deposition temperature. Pure  $\text{Cu}_2\text{O}$  and  $\text{Cu}_3\text{N}$  showed a single phase and smooth morphology only in a narrower temperature range.<sup>15,19</sup>

*The effect of  $\text{H}_2\text{O}$  to  $\text{NH}_3$  ratio on CuON film deposition.*— The deposition rate of CuON depends on the  $\text{H}_2\text{O}$  to  $\text{NH}_3$  ratio at  $140^\circ\text{C}$  as shown in Fig. 4. The deposition rate is mainly determined by the  $\text{H}_2\text{O}$  flow rate, showing that  $\text{H}_2\text{O}$  is more reactive than  $\text{NH}_3$  with the Cu amidinate precursor. Without  $\text{H}_2\text{O}$ , no film was deposited at  $140^\circ\text{C}$ , which shows that the Cu precursor and  $\text{NH}_3$  alone cannot nucleate a  $\text{Cu}_3\text{N}$  film at  $140^\circ\text{C}$ . At substrate temperatures over  $200^\circ\text{C}$ , some  $\text{Cu}_3\text{N}$  film was deposited, but it has a very rough morphology. Thus, CuON film was investigated due to its smoother morphology and higher deposition rate.

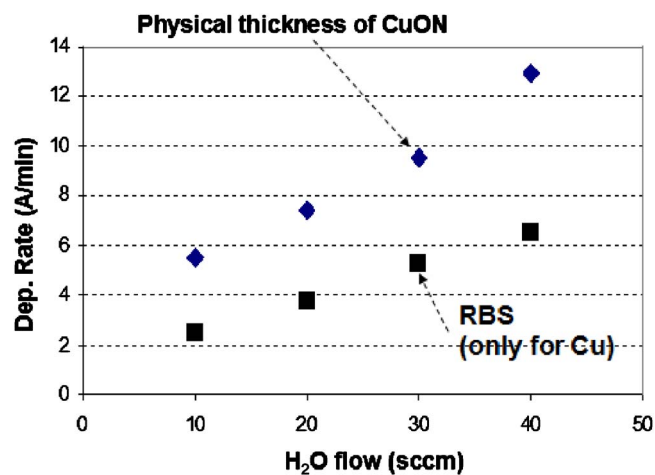




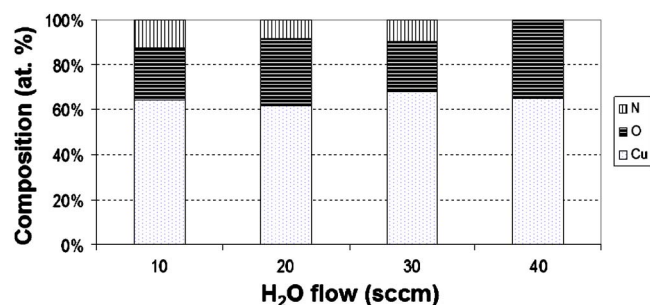
**Figure 2.** (Color online) AFM images of CuON films grown from  $[\text{Cu}(\text{*Bu-Me-amd})_2]$  vapor and a mixture of 30 sccm of  $\text{H}_2\text{O}$  and 10 sccm of  $\text{NH}_3$  at (a) 140, (b) 160, (c) 180, and (d) 220°C, which have about 20 nm thickness.



**Figure 3.** (Color online) The composition of CuON films deposited on carbon substrates from  $[\text{Cu}(\text{*Bu-Me-amd})_2]$  vapor and a mixture of 30 sccm of  $\text{H}_2\text{O}$  and 10 sccm of  $\text{NH}_3$  at different temperatures, as measured by RBS.



**Figure 4.** (Color online) Deposition rate of CuON film at different  $\text{H}_2\text{O}$  and  $\text{NH}_3$  ratios at 140°C, 8 Torr working pressure. Total flow rate of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  is maintained at 40 sccm. Thus, the  $\text{NH}_3$  flow rate is equal to 40 sccm minus the  $\text{H}_2\text{O}$  flow rate.



**Figure 5.** (Color online) Composition of CuON films deposited with different H<sub>2</sub>O to NH<sub>3</sub> ratios at 140°C, 8 Torr working pressure. The NH<sub>3</sub> flow rate is equal to 40 sccm minus the H<sub>2</sub>O flow rate. The composition was measured by RBS from films deposited on amorphous carbon substrates.

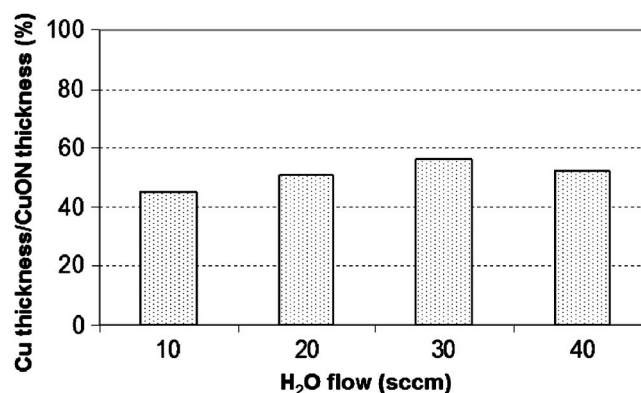
Compositions of CuON films deposited with different H<sub>2</sub>O to NH<sub>3</sub> ratios at 140°C are shown in Fig. 5. The oxygen content of the films exceeds the nitrogen content, even for the film grown from an excess of ammonia (H<sub>2</sub>O to NH<sub>3</sub> flow ratio of 10:30). This is another indicator that water vapor is more reactive with the copper precursor than ammonia is. If we assign the conventional oxidation states to O (−2) and N (−3), these compositions all correspond closely to copper in the +1 oxidation state. Because the copper in the precursor is also in the +1 oxidation state, the reactions with H<sub>2</sub>O and NH<sub>3</sub> do not produce any oxidation or reduction of the copper during CVD of the films.

The “Cu ratio” is defined by the ratio of Cu thickness to physical thickness of CuON. The physical thickness of CuON film was measured by AFM after etching a stripe pattern. Cu thickness was measured by RBS and calculated as if it were pure copper with bulk density. From Fig. 6 the Cu ratio in the CuON films reached a maximum for the conditions of 30 sccm of H<sub>2</sub>O and 10 sccm of NH<sub>3</sub>. Films with a high Cu ratio contain more Cu that may be obtained by the reduction of a given thickness of CuON.

All the CuON films have a very smooth surface morphology. The morphology of deposited CuON depends on the ratio of H<sub>2</sub>O to NH<sub>3</sub> as shown in Fig. 7. With increasing the H<sub>2</sub>O ratio, the grain size increased, but the rms roughness value decreased, so the grains became wider, flatter, and less tall.

The crystal structure of CuON film depended on the ratio of flow rates of H<sub>2</sub>O to NH<sub>3</sub>. The structure was evaluated by electron diffraction in a TEM image (Fig. 8). The diffraction patterns were obtained from CuON films deposited in three different conditions: Fig. 8a for 10 sccm H<sub>2</sub>O and 30 sccm NH<sub>3</sub>, Fig. 8b for 30 sccm H<sub>2</sub>O and 10 sccm NH<sub>3</sub>, and Fig. 8c for 40 sccm H<sub>2</sub>O. The electron diffraction pattern of Fig. 8a (high NH<sub>3</sub>) matches with the Cu<sub>3</sub>N structure.<sup>22</sup> Those of Fig. 8b and c (high H<sub>2</sub>O) coincide with the crystal structure of Cu<sub>2</sub>O.<sup>23</sup> The peak assignments are summarized in Tables I and II for the Cu<sub>3</sub>N and Cu<sub>2</sub>O structures, respectively. Although the CuON films have similar compositions, the films show different crystal structures. The high ratio of NH<sub>3</sub> only makes a Cu<sub>3</sub>N structure, even though that film contains 24 atom % oxygen. The high ratio of H<sub>2</sub>O makes CuON films having only the crystal structure of Cu<sub>2</sub>O. We find no additional diffraction peaks that could arise from a crystalline mixed oxynitride phase, nor did we find any such phases reported. Thus, it seems likely that these films contain a significant amount of amorphous copper oxynitride that only has broad diffraction patterns and a smooth surface morphology.

It is thought that H<sub>2</sub>O reacts with the Cu precursor on a surface, followed by the reaction of NH<sub>3</sub> with Cu–O on the surface because CuON film is not deposited without H<sub>2</sub>O. Thus, a high NH<sub>3</sub> flow and low H<sub>2</sub>O flow make a low deposition rate of Cu<sub>2</sub>O, causing a longer time for NH<sub>3</sub> reaction on the surface, which results in the formation of a Cu<sub>3</sub>N structure containing oxygen. This result coincides with ALD Cu<sub>3</sub>N deposition using a pulse sequence of Cu



**Figure 6.** The ratio of Cu in the CuON film for different H<sub>2</sub>O and NH<sub>3</sub> flow rates. The Cu ratio is defined by the ratio of Cu thickness (from RBS and calculated at the bulk density of Cu) to physical thickness of CuON.

precursor/H<sub>2</sub>O/NH<sub>3</sub>.<sup>16</sup> Torndahl et al.<sup>16</sup> made Cu oxide, first using Cu(hfac)<sub>2</sub> and H<sub>2</sub>O; then it was nitrified by a NH<sub>3</sub> pulse, which resulted in the formation of Cu<sub>3</sub>N. Thus, Cu<sub>2</sub>O and Cu<sub>3</sub>N can be formed by controlling the reaction gas ratio because the kinetic competition between H<sub>2</sub>O and NH<sub>3</sub> with Cu atoms on the surface can make both structures.

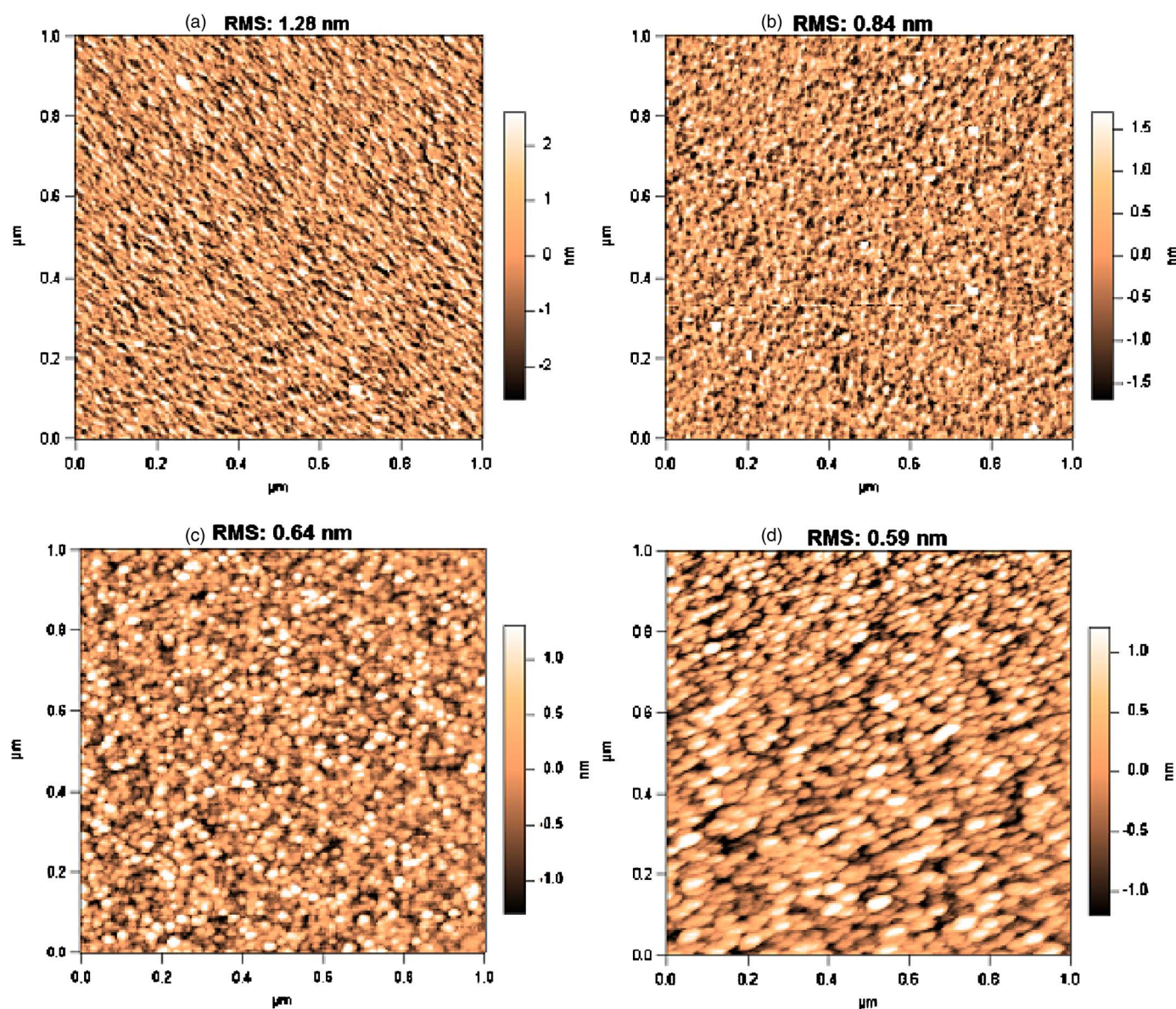
The step coverage of CVD CuON was tested by depositing film on a silicon substrate with holes having aspect ratios of 40:1. The scanning electron microscopy (SEM) image of a cleaved cross section in Fig. 9 shows a step coverage of about 95% at the bottom of these very narrow holes.

*Reduction of CuON with remote H<sub>2</sub> plasma at room temperature.*—CuON films can be deposited with different crystal structures and Cu densities depending on the ratio of H<sub>2</sub>O to NH<sub>3</sub>. The CuON film (high H<sub>2</sub>O CuON) with high H<sub>2</sub>O ratio (H<sub>2</sub>O:30 sccm, NH<sub>3</sub>:10 sccm) has a Cu<sub>2</sub>O crystal structure and a high Cu ratio (53%). Low H<sub>2</sub>O CuON from low H<sub>2</sub>O ratio (H<sub>2</sub>O:10 sccm, NH<sub>3</sub>:30 sccm) has the crystal structure of Cu<sub>3</sub>N and a low Cu ratio (41%). Thus, these two films were used to compare the reduction behavior because these can represent high or low density films. High H<sub>2</sub>O CuON has about a 12% higher Cu ratio than that of low H<sub>2</sub>O CuON.

The CuON films were reduced with remote H<sub>2</sub> plasma. The films were not heated deliberately, but their temperature did rise from room temperature to about 50°C because of the heat released by the recombination of hydrogen atoms to form H<sub>2</sub> and by reaction with oxygen and nitrogen on CuON surfaces. The as-deposited thicknesses of these high H<sub>2</sub>O CuON and low H<sub>2</sub>O CuON films were 16 and 14 nm, respectively. The sheet resistance of the films depends on reduction time as shown in Fig. 10. After 1 min reduction treatment, both CuON films were reduced to Cu. The sheet resistance is not changed further after 3 min reduction, which means that reduction for 1 min is sufficient to reduce 14–16 nm thick CuON films with either crystal structure. The morphology of reduced CuON was evaluated by AFM, shown in Fig. 11. Both high H<sub>2</sub>O and low H<sub>2</sub>O CuON showed smooth surface morphology (1.1–1.2 nm rms roughness) even after 3 min reduction. Thus, the reduced Cu films were not agglomerated even at a longer reduction time. Because the films retain their smooth morphology even after over-reduction for longer times, we expect that films can also be reduced successfully inside the whole length of deep trenches. Film near the top of a trench will be reduced before film deeper in the trench, which only receives a smaller flux of hydrogen atoms depleted by reactions at the walls during their diffusion down the trench.

Because these films were reduced at nearly room temperature, they can maintain their smooth surface morphology by avoiding diffusion of the Cu over the Ru surface to form agglomerates. How-





**Figure 7.** (Color online) AFM image of CuON film grown at 140°C with the flow rate of H<sub>2</sub>O and NH<sub>3</sub>; (a) 10:30, (b) 20:20, (c) 30:10, and (d) 40:0 sccm.

ever, CuON films deposited on SiO<sub>2</sub> underlayers were agglomerated under the same reduction condition, as shown by the increase in rms roughness from 0.7 to ~3.5 nm (Fig. 12). Any surface oxide on ruthenium can be reduced during the CuON reduction because the stabilities of Cu<sub>2</sub>O and RuO<sub>2</sub> are similar. The Gibbs energies of the reduction reactions for these oxides are similar,<sup>21</sup> which implies both metal oxides can be reduced under similar reduction conditions. The Cu is bonded strongly to the reduced metallic surface of Ru. However, Cu on Si having a native oxide can be agglomerated during reduction even at room temperature due to the high mobility of Cu atoms on oxide surfaces<sup>9</sup> and the difficulty of reducing silicon oxides. Thus, an easily reducible underlayer like Ru is essential for maintaining a smooth surface morphology during the reduction of CuON.

The volume shrinkage of two CuON films was evaluated by comparing the thickness of CuON film before and after reduction. The physical thickness of high H<sub>2</sub>O CuON is changed from 16 to 9 nm, which is a shrinkage of volume by 45%. Low H<sub>2</sub>O CuON showed that the thickness is changed from 14 to 7 nm, which means a 50% volume shrinkage. These samples are evaluated by RBS to measure the density of reduced Cu film. The RBS result shows that

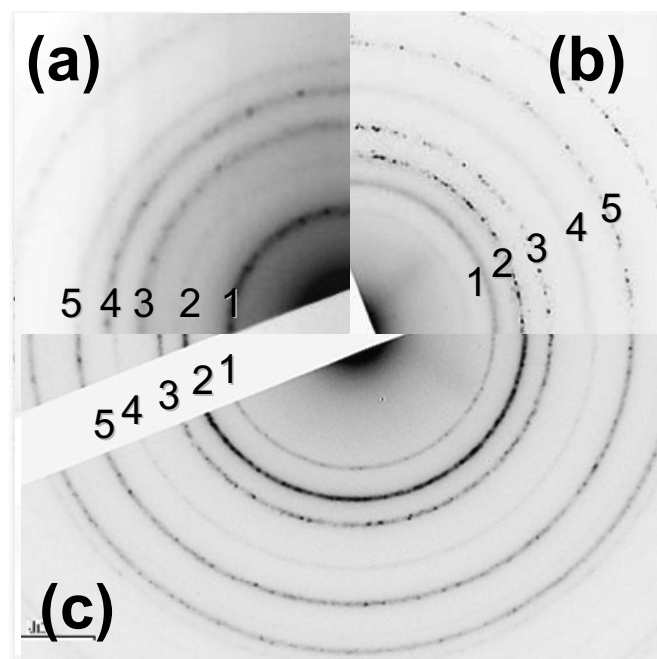
the thickness of high or low H<sub>2</sub>O CuON would be 8.5 or 5.9 nm, respectively, if they had bulk Cu density. Thus, comparing these values with the physical thicknesses, the density of the reduced copper from high Cu<sub>2</sub>O CuON or low H<sub>2</sub>O CuON is 95 or 84%, respectively, of the bulk value. Summarizing the density of the CuON films, high Cu<sub>2</sub>O CuON has a higher density not only in the as-deposited film but also after reduction. Thus, high Cu<sub>2</sub>O CuON film should be used as the most suitable Cu compound for reduction to deposit a dense, reduced Cu film.

The resistivity of reduced high Cu<sub>2</sub>O CuON is 12 μΩ cm at a thickness of 9 nm. That of low H<sub>2</sub>O CuON film has 15 μΩ cm at a thickness of 7 nm. These values are similar to the resistivity of sputtered Cu at the corresponding thicknesses.<sup>15</sup> Thus, the reduced Cu film has a high density and high purity.

All the reduced copper films on ruthenium pass the tape test for adhesion, whereas the ones on silica are easily pulled off by tape. More quantitative 4-point bend tests of adhesion are underway.

### Conclusions

Smooth, continuous, dense, and conformal Cu films with ~1 nm rms roughness and thickness <10 nm were fabricated by



**Figure 8.** TEM diffraction pattern of CuON films grown at 140°C with the flow rate of H<sub>2</sub>O and NH<sub>3</sub> at (a) 10:30, (b) 30:10, and (c) 40:0 sccm.

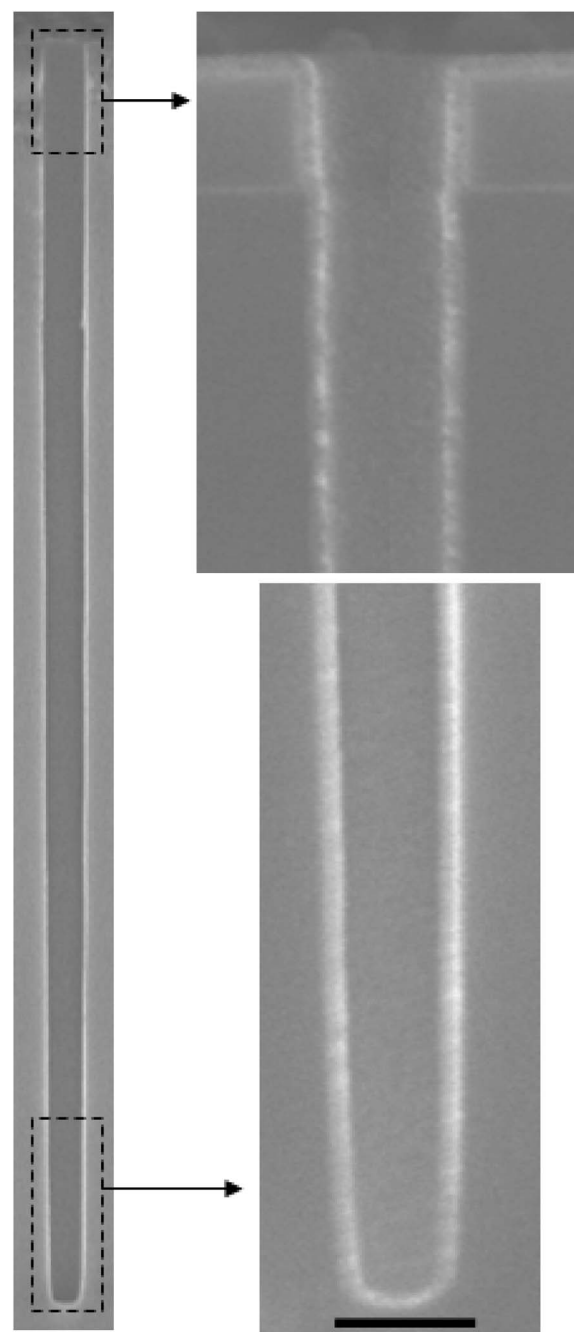
CVD of CuON followed by reduction with remote hydrogen plasma at room temperature. The crystal structure of CuON can be controlled by the ratio of H<sub>2</sub>O and NH<sub>3</sub>, although the elemental composition of the film was not changed significantly. A high H<sub>2</sub>O ratio makes the CuON film having a Cu<sub>2</sub>O crystal structure. A low H<sub>2</sub>O ratio, meaning high NH<sub>3</sub> partial pressure, makes CuON films having a Cu<sub>3</sub>N crystal structure. The reduction rate of the films does not show any difference depending on the crystal structure. CuON film with a Cu<sub>2</sub>O structure produces a higher density of Cu after reduction. Thus, CuON having a Cu<sub>2</sub>O structure is the best Cu compound

**Table I.** Electron diffraction results for low H<sub>2</sub>O CuON film from TEM. The index of plane (*hkl*) and interplanar spacing (*d*) shown in this table represents the Cu<sub>3</sub>N crystal structure. Error means the difference between reference data and measured data.

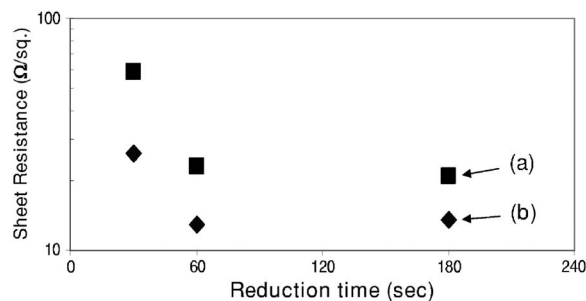
No.	<i>hkl</i>	<i>d</i> (Å)	Int.	Measured <i>d</i> (Å)	Error (%)
1	100	3.82	60	3.83	-0.26
2	110	2.70	30	2.69	0.21
3	111	2.20	100	2.20	-0.02
4	200	1.91	80	1.91	-0.29
5	210	1.71	30	1.69	0.89

**Table II.** Electron diffraction result for high H<sub>2</sub>O CuON film from TEM. The index of plane (*hkl*) and interplanar spacing (*d*) shown in this table represents the Cu<sub>2</sub>O crystal structure. Error means the difference between reference data and measured data.

No.	<i>hkl</i>	<i>d</i> (Å)	Int.	Measured <i>d</i> (Å)	Error (%)
1	110	3.04	20	3.03	0.32
2	111	2.46	100	2.46	0.04
3	200	2.14	70	2.14	-0.13
4	211	1.74	20	1.74	-0.24
5	220	1.51	90	1.50	0.66



**Figure 9.** SEM image of a CuON film deposited at 140°C with 30 sccm of H<sub>2</sub>O and 10 sccm of NH<sub>3</sub> on an oval hole (diameter 0.13 × 0.19 μm, length 6.7 μm). Scale bar is 200 nm.



**Figure 10.** Sheet resistance of (a) low and (b) high H<sub>2</sub>O CuON film depending on reduction time at room temperature.



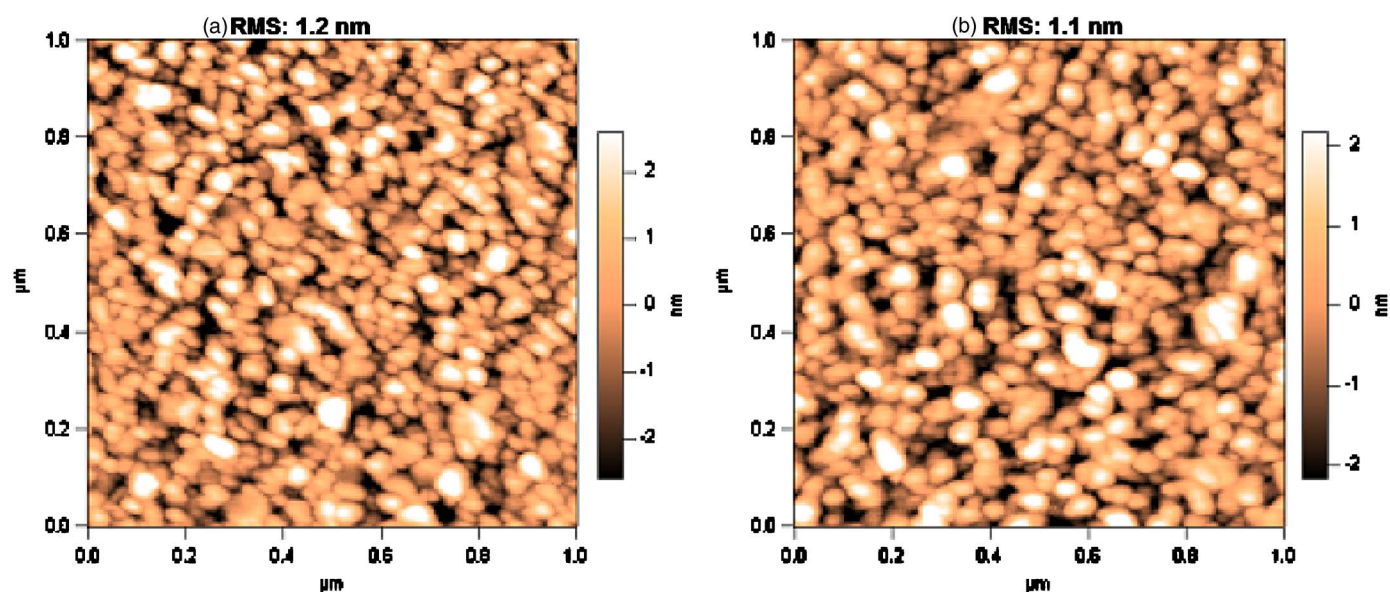


Figure 11. (Color online) AFM image of reduced Cu films from (a) low and (b) high  $\text{H}_2\text{O}$  CuON at room temperature for 3 min on Ru substrates.

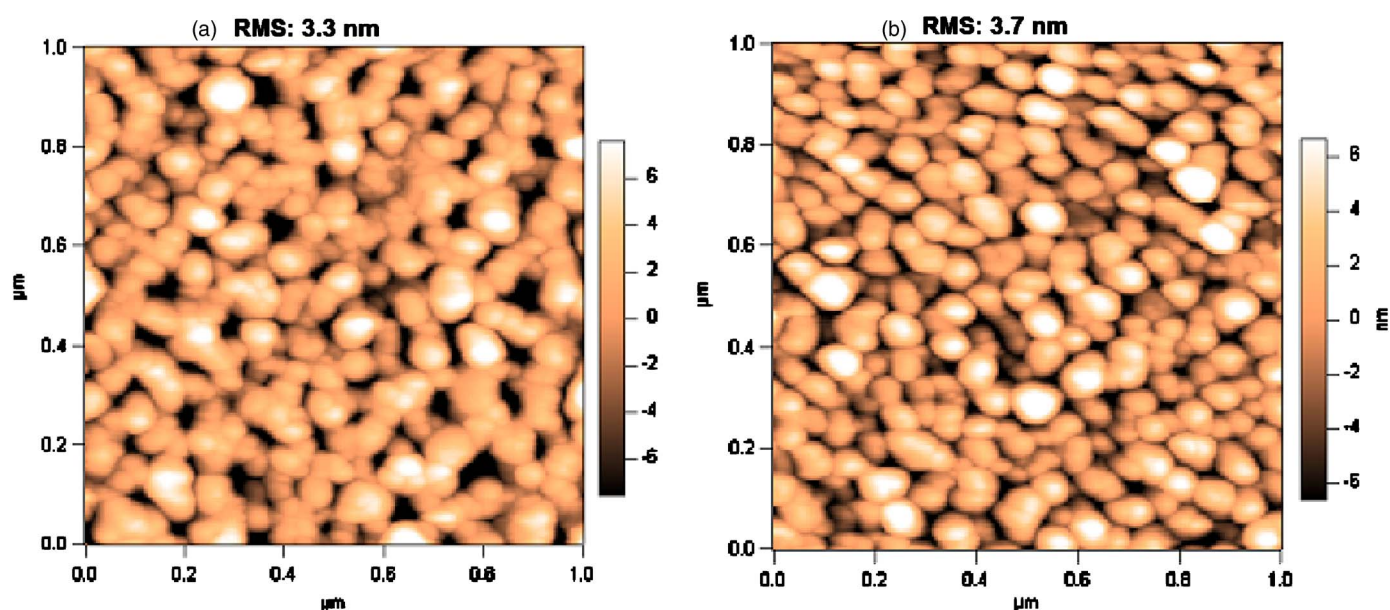


Figure 12. (Color online) AFM image of reduced Cu films from (a) low and (b) high  $\text{H}_2\text{O}$  CuON at room temperature for 3 min on  $\text{SiO}_2$  substrates.

for this deposition and reduction process, which is a promising method for Cu seed layer deposition for future Cu interconnects.

#### Acknowledgments

The copper precursor was supplied by the Advanced Thin-Film Technologies Group, Rohm and Haas Electronic Materials. Silicon substrates with deep trenches were supplied by Qimonda. Support for this work was provided by the Rohm and Haas Company, Intel Corporation, and the National Science Foundation.

Harvard University assisted in meeting the publication costs of this article.

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